METAL PARTS FURNACE

SPRAY TANK
DEMONSTRATION TEST PLAN

Appendix B

ESTIMATION OF LEAD EMISSION RATES AND CONCENTRATIONS

Revision 2

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ESTIMATION OF LEAD EMISSION RATES AND CONCENTRATIONS

The TMU-28/B spray tanks are part of the bulk Agent VX containers at the Deseret Chemical Depot (DCD). Spray tanks were designed to be mounted on aircraft. The pilot would open the spray tank at the designated time and disperse the contents of the spray tank. The lead in the nose cone allows aircraft to carry the tank underneath the plane and minimize handling problems for the pilot.

Each spray tank is approximately 136 inches in length and 22.5 inches in diameter. Spray tanks are equipped with a compartment at the tip of each spray tank (nose cone). The nose cone contains 81 lbs. of lead, a polyethylene covering on the lead, a 1 inch by 0.050 inch thick polyethylene ring gasket and a stainless steel retaining ring insert. The insert is spot welded to the outer skin to retain the lead in a tight fit within the nose cavity. Small amounts of water may also be present in the nose cone. Paint on the exterior of the spray tanks will add 1.59 pounds of lead to each spray tank. The total lead for each spray tank is 82.59 pounds.

Initial testing of the nose cone assembly was conducted for the Army in 1994 (1). A copy of the final report is included as Appendix C to this Plan. This testing indicated that the nose cones could rupture and discharge molten lead into the furnace if a pressure relief vent was not established (1). The solution to this problem is to drill a 3/8-inch hole in the nose cone to prevent pressure buildup. This vent hole becomes an exit for pyrolysis gases, water vapor, and lead vapor.

The plan for decontaminating these spray tanks filled with Agent VX is to drain the tanks to a minimal heel (less than 5%). A hole will be drilled in the nose cone to prevent the build up of pressure in the nose cone when heating the spray tank. The spray tanks will then be sent to the Metal Parts Furnace (MPF) to thermally destroy the remaining Agent VX. The MPF performance when processing spray tanks will be demonstrated with a MPF Spray Tank Demonstration Test (STDT).

This document was prepared to estimate the lead emission rates to show that conducting the STDT will not endanger human health or the environment. Lead vapor exiting the nose cone becomes part of the exhaust gases and could be emitted to the environment. The planned approach was to calculate an estimated lead emission rate and concentration. The estimated results would then be compared to the emission rate used in the Screening Risk Assessment (SRA) developed in 1996, the DCD Human Health Risk Assessment (HHRA) developed in 2002, and to the EPA Maximum Achievable Control Technology (MACT) concentration limit for lead. If the calculated emission rates and concentrations were below values used in the SRA, HHRA, and MACT, the lead emissions would be considered to be at a safe level. These estimated emission rates would be the safety basis for conducting the STDT.

An estimate of the lead emissions would result from three different processes. One process is the volatilization of lead in the paint on the exterior surface of the spray tank. The other two methods involve the migration of lead from the spray tank nose cone. One migration method is for the lead to diffuse out of the nose cone. This method would be the method of control in the absence of any additional motive forces that can carry lead out of the nose cone. The plastic parts within the nose cone provide the second migration method for moving lead from the nose cone. Heating the plastic will cause the polyethylene to pyrolyze into shorter chain carbon compounds. This decomposition causes gases to be formed that will stream out of the nose cone through the drilled hole. Gases exiting the nose cone would carry lead in the vapor phase out into the furnace. The estimate of lead emissions will be a combination of the three methods. Each method is described below.

DIFFUSION OF LEAD FROM THE NOSE CONE

The calculated emission rate for diffusion of lead from the nose cone was taken from Fick's First Law of Diffusion (2). The equation used for the emission rate is:

$$\text{Emission rate (ER), g/sec} = D * a * dC/dx$$

Where:

D = Diffusivity of lead
a = area of opening
dC = Change in concentration
dx = change in distance for concentration change

The MPF will process spray tanks at 1,525 °F, which is 829 °C or 1,102 °K.

The diffusivity for lead was taken from data in Table 2-381, page 2-336 of Perry's Chemical Engineering Handbook (3).

$$D = 1.5 \times 10^{-5} \ \text{m}^2/\text{sec} = 0.15 \ \text{cm}^2/\text{sec}$$

The area of a 3/8-inch hole is:

$$\text{Area} = \pi r^2 = \pi * [(0.375 \text{ in.} * 2.54 \text{ cm/in.})/2]^2 = 0.713 \text{ cm}^2$$

The nose cone encloses the lead; therefore, the thickness of the nose cone metal was taken as the distance of the concentration gradient, dx.

$$dx = 0.020 \text{ inch} = 0.020 \text{ in.} * 2.54 \text{ cm/in.} = 0.0508 \text{ cm}$$

The lead concentration inside the nose cone is based on the vapor pressure (VP) of lead at the MPF operating temperature of 1,525 °F. The lead VP @ 1,525 °F was calculated from data in Table 2-7, page 2-58 from Perry's Handbook (3). The data on the VP of lead is plotted in Figure B-1. A linear regression was developed using the three lowest temperatures to calculate the lead VP at 1,525 °F. Lead VP @ 1,525 °F was calculated to be 0.174 mm Hg. The assumption was made that the lead vapor follows the Ideal Gas Law and the concentration was calculated as follows:

$$PV = nRT \Rightarrow n/V = P/RT$$

$$n/V = \frac{(0.174 \text{ mm Hg})}{[(62{,}400 \text{ mm Hg} - \text{cm}^3/\text{mole °K}) * (1102 \text{ °K})]}$$

$$n/V = 2.53 \text{ X } 10^{-9} \text{ mole/cm}^3$$

$$\text{Pb Conc., g/cm}^3 = (2.53 \text{ X } 10^{-9} \text{ mole/cm}^3) * (207.19 \text{ grams/mole})$$

$$\text{Pb Conc., g/cm}^3 = 5.24 \text{ X } 10^{-7} \text{ g/cm}^3$$

The assumption was then made that the lead concentration outside the nose cone would be approximately zero when compared to the lead concentration inside the nose cone. Therefore, the change in concentration (dC) would be equal to the concentration within the nose cone or 5.24 X 10^{-7} g/cm^3 at the opening in the nose cone.

The lead emission rate was then calculated using the equation:

$$ER = D * a * dC/dx$$

$$ER = (0.15 \text{ cm}^2/\text{sec}) * (0.713 \text{ cm}^2) * (5.24 \text{ X } 10^{-7} \text{ g/cm}^3) / (0.0508 \text{ cm})$$

$$ER = 1.103 \text{ X } 10^{-6} \text{ g/sec for 1 spray tank}$$

The ER will be 2.21 X 10^{-6} g/sec since there are two spray tanks in the MPF most of the time.

The diffusion ER was used to calculate the mass of lead emitted from the nose cone of the spray tank. Spray tanks will spend 43 minutes in Zone 1 and 24 minutes in Zone 2 for a total of 67 minutes (4,020 seconds) in the heated zones. The mass emitted from each spray tank was calculated to be 4.42 X 10^{-3} grams using the following equation:

$$\text{Mass emitted by Diffusion } (M_D)\text{, grams} = ER * t; \quad \text{Where } t = 4{,}020 \text{ seconds}$$

$$M_D\text{, grams} = 1.103 \text{ X } 10^{-6} \text{ grams/sec} * 4{,}020 \text{ seconds} = 4.43 \text{ X } 10^{-3} \text{ grams}$$

M_D, milligrams = 4.43 milligrams

M_D, pounds = 4.43 X 10 $^{-3}$ grams * (1 pound/453.59 grams) = 9.77 X 10 $^{-6}$ pounds

The mass emitted is very little when compared to the 81 pounds in the nose cone.

LEAD CARRY OUT BY PYROLYSIS GASES

The second method of moving lead emissions from the nose cone is by the creation of gases within the nose cone and their expansion outside the nose cone. The material listed as contained in the nose cone (1) included water and plastic. The pressure used in these calculations was the atmospheric pressure corrected for the pressure in the MPF. The pressure data was taken during the MPF Agent VX Trial Burn which was 24.90 inches of mercury (in.Hg) and an internal MPF pressure of -5 inches of water (in.H_2O). The system pressure was converted to 0.8322 atmospheres (atm) using the following calculations:

P_{atm} = 24.90 in.Hg / (29.92 in.Hg/atm) = 0.8322 atm

P_{MPF} = -5 in.H_2O * 0.0735559 in.Hg/in.H_2O * 1 atm/(29.92 in.Hg)
= -0.0123 atm

P = 0.8322 atm + (-0.0123 atm) = 0.8199 atm

The increase in volume from evaporating the 2 grams of water found in the nose cone was calculated as follows:

$PV = nRT \Rightarrow V = nRT/P$

V_W = [(2 grams/18 grams/mole) * (0.08205 atm * liters/(mole * °K)) * (1102 °K)]/0.8199 atm

V_W = 12.25 liters

The generation of gases from the pyrolysis of polyethylene was calculated from the mass of plastic identified in the nose cone (1) and assuming that ethylene was generated by the decomposition for calculation purposes. The volume of ethylene was then estimated. The following calculations were made:

Mass plastic = 81 cm^3 * 0.92 grams/cm^3 = 74.52 grams

Assumed 74.52 grams of polyethylene was converted to 74.52 grams of ethylene with a molecular weight of 28 grams/mole. The volume was calculated as follows:

$V_e = nRT/P$

$V_e = [(74.52 \text{ g}/28 \text{ g/mole}) * (0.08205 \text{ atm} * \text{liters}/(\text{mole} * °K)) * (1102 °K)]/0.8199 \text{ atm}$

$V_e = 293.5$ liters

The total volume was taken as the volume from water and from ethylene.

$V_T = V_w + V_e = 12.25 \text{ liters} + 293.5 \text{ liters} = 305.8 \text{ liters}$

The lead concentration in the nose cone was assumed to be based on the vapor pressure of lead at 1,525 °F. The total mass of lead emitted was then calculated from the volume of gas exiting the nose cone and the lead concentration within the nose cone.

Mass emitted from Gas Evolution (M_{GE}), grams = Pb conc. * V_T

M_{GE}, grams = $(5.24 \times 10^{-7} \text{ g/cm}^3) * (10^3 \text{ cm}^3/\text{liter}) * (305.8 \text{ liters}) = 0.1602$ grams

The lead emission rate was then calculated from the lead mass and the time the emission occurs over using the following calculation:

ER = (0.1602 grams) / (67 minutes * 60 seconds/minute) = 3.986×10^{-5} g/sec

Two spray tanks will be present in the MPF so the total ER from gas generations will be 7.97×10^{-5} g/sec.

TOTAL LEAD EMISSIONS FROM THE NOSE CONE

An ER for the nose cone was then summed from the diffusion of lead from the nose cone and the lead carried from the nose cone by the expansion of gases (ER_{NC}).

$ER_{NC} = 2.21 \times 10^{-6} \text{ g/sec} + 7.97 \times 10^{-5} \text{ g/sec} = 8.19 \times 10^{-5} \text{ g/sec}$

The ER_{NC} represents the metal emissions exiting the Primary Combustion Chamber (PCC) of the MPF from the nose cone. The Pollution Abatement System (PAS) will remove a large fraction of the lead exiting the PCC. The Metals Removal Efficiency (MRE) for this process was estimated to be similar to the MRE demonstrated by the LIC Metals Demonstration Test. The measured MRE for the LIC MDT was 99.983 %. This MRE was applied to the ER_{NC} to calculate the estimated emission rate from the stack (ER_{NCS}) based on nose cone emissions. The ER_{NCS} was calculated to be 1.37×10^{-8} g/sec based on the following calculation:

$ER_{NCS} = ER_{NC} * (1-0.99983) = (8.19 \times 10^{-5} \text{ g/sec}) * (0.00017) = 1.39 \times 10^{-8} \text{ g/sec}$

LEAD EMISSIONS FROM PAINT ON THE SPRAY TANKS

Lead emissions will also result from the lead in the paint on the exterior of the spray tanks. Each spray tank has 1.59 pounds of lead in the paint. The spray tanks are fed at a rate of 1.4 spray tanks per hour, which gives a lead feed rate of 2.23 pounds per hour. Lead was spiked into the MPF feed for the Agent GB ATB. The measured MRE for the MPF GB ATB was greater than 99.99 %. The MRE from the LIC MDT of 99.983 % was used for the calculation of an ER for the paint in the MPF STDT. An ER for the paint (ER_P) was calculated to be 6.19×10^{-8} g/sec based on the following calculations:

Feed Rate = (1.59 lbs./spray tank) * (1.4 spray tanks/hr) = 2.23 lbs./hr

ER_P = (2.23 lbs./hr) * (1 hr/3600 sec) * (1 - 0.99983) = (2.23 lbs./3600 sec) * (0.00017)

$$ER_P = 1.05 \times 10^{-7} \text{ g/sec}$$

TOTAL LEAD EMISSIONS FROM SPRAY TANKS

A total ER was calculated by summing the ER_{NCS} and the ER_P and was found to be 1.19×10^{-7} g/sec based on the following calculation:

$$ER_T = ER_{NCS} + ER_P = 1.39 \times 10^{-8} \text{ g/sec} + 1.05 \times 10^{-7} \text{ g/sec} = 1.19 \times 10^{-7} \text{ g/sec}$$

The total concentration of lead in the MPF Duct was calculated from the total emission rate:

$$Pb_{conc} = ER/GFR$$

Where: GFR = Gas Flow Rate = 4,953 ft^3/min from MPF VX ATB

$$Pb_{conc} = (1.19 \times 10^{-7} \text{ g/sec}) * (60 \text{ sec/min}) * (1 \text{ min}/4953 \text{ ft}^3) * (35.315 \text{ ft}^3/\text{m}^3) * (1 \times 10^6 \ \mu\text{g/g})$$

$$Pb_{conc} = 0.0509 \ \mu\text{g/m}^3$$

The lead concentration was corrected to 7% O_2 using the O_2 concentration from the MPF GB ATB of 13.1 %.

$$Pb_{conc} \text{ @ } 7\% \ O_2 = (0.0509 \ \mu\text{g/m}^3) * [14/(21-13.1)] = 0.0902 \ \mu\text{g/m}^3$$

COMPARISON OF RESULTS

The calculated emission rates and concentrations were compared to emission rates used for the SRA and the HHRA. The concentration calculated was compared to the MACT limit for lead and the reporting limit for the method.

$ER_T = 1.19 \text{ X } 10^{-7}$ g/sec

SRA ER = $4.15 \text{ X } 10^{-4}$ g/sec

SRA ER / ER_T = 3,487

HHRA ER = $8.95 \text{ X } 10^{-6}$ g/sec

HHRA ER / ER_T = 75

Reporting Limit ER = $7.3 \text{ X } 10^{-7}$ g/sec

Reporting Limit Pb_{conc} @ 7% O_2 = 0.4 $\mu g/m^3$

Pb_{conc} @ 7% O_2 = 0.0879 $\mu g/m^3$

$MACT_{limit}$ = 240 $\mu g/m^3$ @ 7% O_2

It should be noted that the reporting limit for the metal emissions sampling is higher than the estimated concentration of lead from the MPF while processing spray tanks. The reporting limit is a factor of 10 lower than the HHRA ER.

The total mass estimated to leave each nose cone was a sum of the mass leaving by gas generation and from the mass diffusing from the nose cone. The total mass of 0.1646 grams (0.00036 lbs.) is very small when compared to the 81 pounds of lead in the nose cone.

Mass Total (M_T), grams = $M_D + M_{GE}$

M_T , grams = 0.00443 grams + 0.1602 grams = 0.1646 grams

CONCLUSION

Lead emission rates and lead concentrations in the exhaust gases have been evaluated and were determined to be at safe levels. The emission rates were estimated to be less than the emission rates used in the SRA and the HHRA. The estimated total emission rate is a factor of 75 less than the TOCDF MPF Weighted Emission rate for lead from the DCD Human Health Risk Assessment. Lead concentrations in the exhaust gases are estimated to be a factor of 2,700 less than the MACT interim limits published.

Based on this evaluation, the data generated during the MPF STDT will be able to show the lead emission rate is not a threat to human health or the environment. Lead in the nose cone should be considered to be embedded since it is estimated that less than 0.2 grams of the 81 pounds (36,741 grams) is emitted from the nose cones.

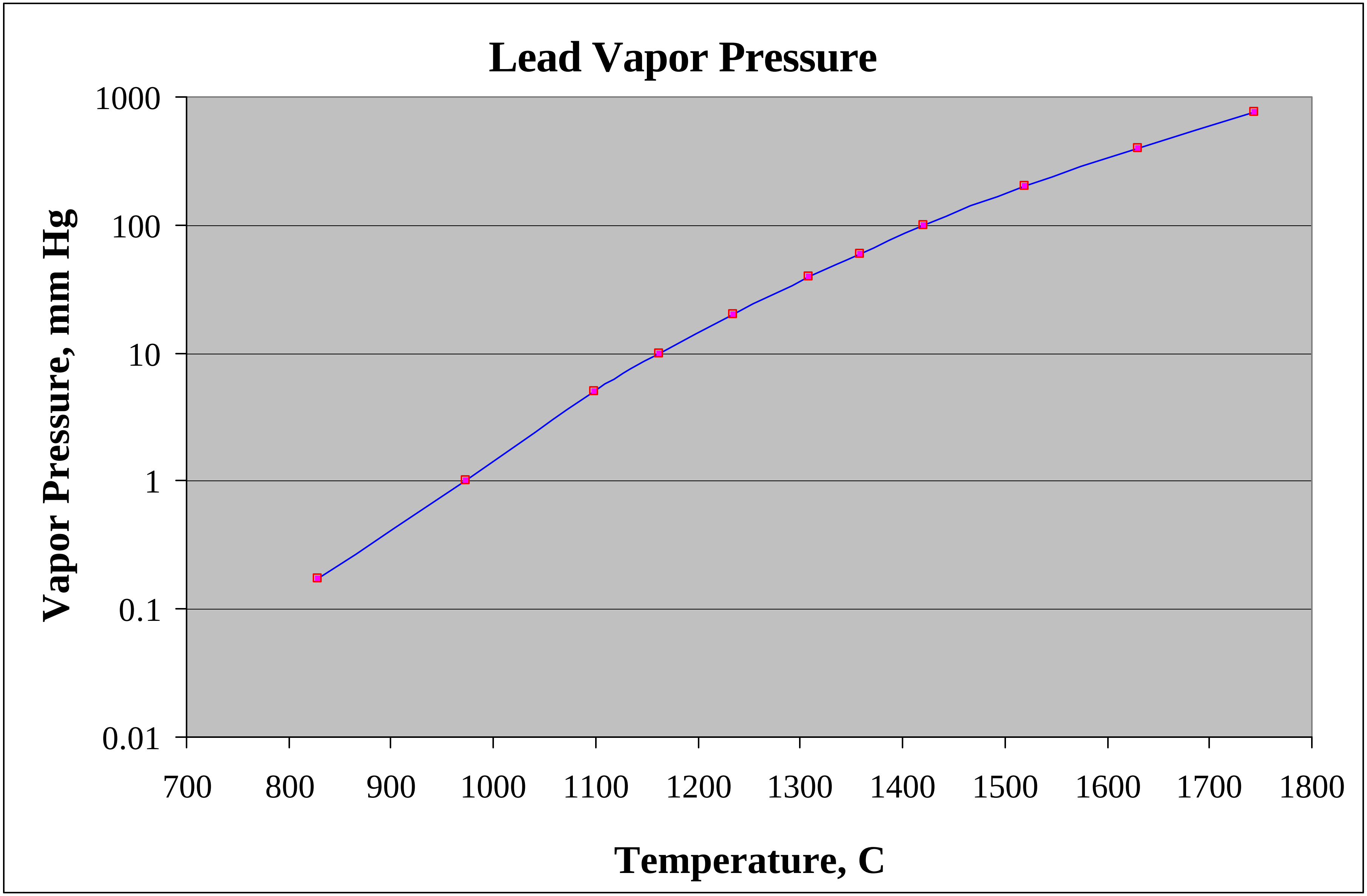
REFERENCES

(1) ***RESULTS OF TMU-28 SPRAY TANK NOSE CONE TEST***, Final Report, HY-TEK Mfg. Co. Inc., January 1994. (Copy included in Appendix B)

(2) Moore, Walter J., ***Physical Chemistry***, 4th Edition, Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1972, pp. 159-164.

(3) ***Perry's Chemical Engineering Handbook***, 7th Edition, McGraw-Hill, New York, New York, 1998.

Figure B-1.


Lead Vapor Pressure
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100
10
1
0.1
0.01
Vapor Pressure, mm Hg
700
800
900
1000
1100
1200
1300
1400
1500
1600
1700
1800
Temperature, C